not significantly different ($F = 2.20$; df = 1, 30; $P = 0.138$). The average trap catch in the control orchard continued to increase after this to a peak of 622 on the fifth week of spraying, while the average trap catch in the treatment orchard dropped during the week after the first spray and never exceeded 100 throughout the rest of the study (Fig 1A). The average trap catch in the treatment orchard was always significantly less than in the control orchard from the second week of spraying through the week after the last spray.

3.2 Fruit infestation

As of the first week of spraying, the average oriental fruit fly infestation (including parasitoids which had parasitized eggs or larvae of oriental fruit fly) was not significantly different in the treatment orchard (70.8 flies kg^{-1} guava) and in the control orchard (47.7 flies kg^{-1} guava) ($F = 2.09$; df = 1.16; $P = 0.168$). Fruit infestation subsequently dropped in both orchards, but the decrease was greater in the treatment orchard, so that the infestation there was significantly less on the 3rd, 5th, 7th, 8th, 9th and 11th weeks of spraying (Fig 1B), by which time the protein bait trap catches showed that the population level in the control orchard had fallen considerably (Fig 1A). Percentage parasitization of oriental fruit fly by *Biosteres arisanus* (Sonan) was typically higher in the treatment orchard throughout the study, averaging 55.1% in the treatment orchard over the last seven spray weeks, compared to 42.1% in the control orchard (Fig 1B), suggesting that the bait sprays were not adversely affecting the population of this parasitoid.

The results presented here suggest that phloxine B-protein bait sprays can suppress established oriental fruit fly populations and that phloxine B is a potential replacement for malathion in bait sprays for tephritid fruit fly suppression/eradication programs. However, more extensive tests are needed which limit immigration of adult flies and parasitoids from surrounding unsprayed areas.

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Synthesis and herbicidal activity of new benzenesulfonylureas

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Abstract: A series of benzenesulfonylurea derivatives possessing a branched hydroxymethyl moiety as an *ortho*-substituent were synthesized and found to have interesting herbicidal activity under submerged paddy conditions.

Keywords: benzenesulfonylureas; branched hydroxymethyl; K11451; submerged paddy conditions

In 1982, DuPont disclosed a patent[1] covering new benzenesulfonylurea herbicides possessing a hydroxymethyl sub-unit. However, the biological data in the patent did not indicate any distinct characteristics in terms of herbicidal activity and crop tolerance.

Recently, we developed a new synthetic method for sulfonylchlorides that could be utilized for the synthesis of a variety of sulfonylurea compounds.[2] During the programme aimed at developing a new type of sulfonylurea herbicide, we synthesized a series of benzenesulfonylurea derivatives possessing a branched hydroxymethyl moiety as an *ortho*-substituent, employing the new method and procedures from the literature[3] and found that the compounds had interesting herbicidal activity (Fig 1; Table 1).[4]

In method A (Fig 1) *o*-bromophenyl methoxymethyl sulfide was lithiated using *n*-butyl lithium by a metal–halogen exchange reaction and reacted with an electrophile. The resulting hydroxyalkyl-sybstituted phenyl methoxymethyl sulfide was protected using acetic anhydride (carbonyl compounds were reduced before protection) and the protected sulfide was then converted into the corresponding sulfonamide via successive chlorination-amination reactions. The sulfonamide was then coupled with carbamate, using a conventional method, and the acetyl group was

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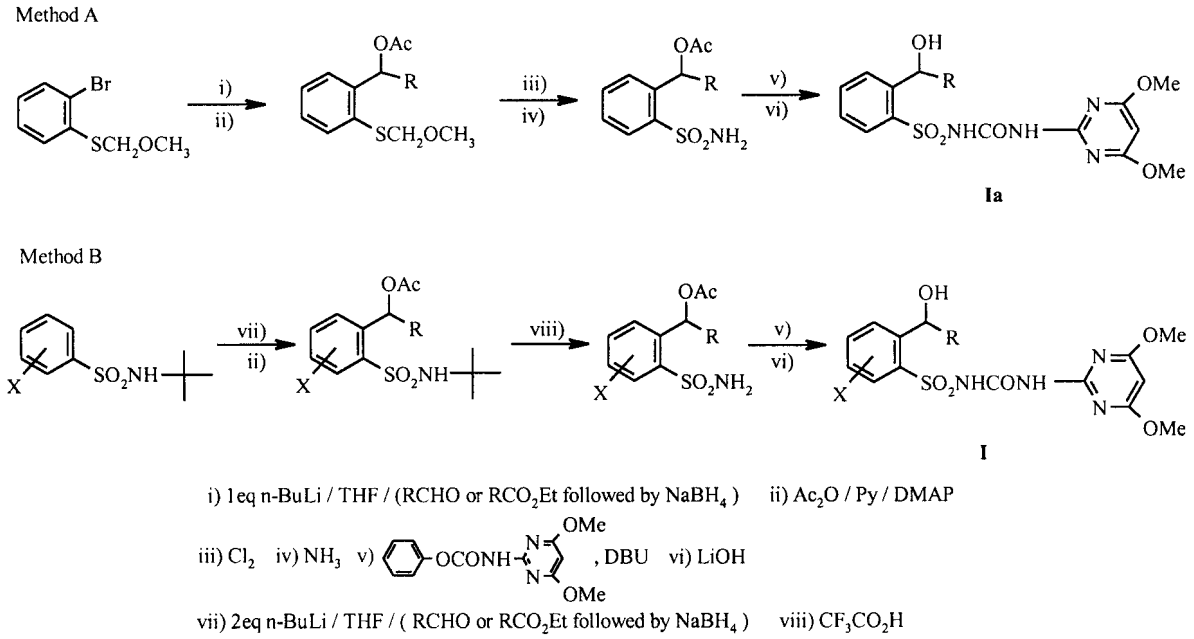

Figure 1. Synthetic schemes for benzenesulfonylureas.

				Activity[a] *against*		
Compound	*X*	*R*	*Rate* ($g\,ha^{-1}$)	*ORYSA*[b]	*ECHOR*[c]	(*Other paddy weeds*[d] *average control*)
1	H	H	50	60	70	70
2	H	CH_3	6	100	100	100
3	H	CH_2OCH_3	50	100	100	100
			6	90	90	95
4	H	CH_2F	50	100	100	100
			3	70	100	100
5	H	CH_2Cl	50	70	90	93
			3	20	0	53
6	H	CHF_2	50	60	90	68
7[e]	H	$CHFCH_3$	50	80	100	100
		(*Erythro*)	12	20	100	99
			3	0	70	90
8	H	$CHFCH_3$	50	60	100	75
		(*Threo*)	12	10	80	88
			3	0	50	75
9	6-F	$CHFCH_3$[f]	50	60	100	92
			3	20	70	88
10	6-$N(CH_3)_2$	$CHFCH_3$[f]	50	0	90	68
11	5-F	$CHFCH_3$[f]	50	0	0	0
12	5-OCH_3	$CHFCH_3$[f]	50	70	100	90
			3	0	50	30
13	3-F	$CHFCH_3$[f]	50	10	50	68
14	4-F	$CHFCH_3$[f]	50	40	70	83

[a] 0: no effect, 100: complete control.
[b] ORYSA: *Oryza sativa* three-leaf stage of rice seedling.
[c] ECHOR: *Echinochloa crus-galli*.
[d] Other paddy weeds: *Scirpus juncoides, Monochoria vaginalis, Cyperus serotinus, Sagittaria pygmaea*.
[e] Code number: **K11451**.
[f] Of the two isomers, the more active compound is shown. Stereochemistry of each compound was not assigned.

Table 1. Herbicidal activity of sulfonylureas **1** under submerged paddy conditions

removed, using lithium hydroxide, to afford compound **1a**.

For substitution on the phenyl ring we started with *tert*-butyl benzenesulfonamide derivatives, employing a literature procedure.[3] An electrophile was introduced into the *ortho*-position of the sulfonyl group using carbanion chemistry. Protection of the resulting hydroxy group, followed by de-protection of the *tert*-butyl group with trifluoromethyl acetic acid provided a sulfonamide which could be converted to various sulfonylurea compounds with a substituent on the phenyl ring, as shown in Method B (Fig 1).

Comparison of the herbicidal activities of compound **1**, with no branching, and compound **2** indicates that introduction of a methyl group results in a considerable increase in herbicidal activity (Table 1); however, compound **2** does not show selectivity towards rice. Compound **4**, with a monofluoromethyl group, has similar activity to compound **2** but shows less damage to rice. Replacement of a monofluoromethyl with a difluoromethyl or a monochloromethyl group (compounds **5** and **6**, respectively) results in decreased herbicidal activity.

Introduction of a fluoroethyl group produces the two diastereoisomers **7** and **8** which can be separated easily by chromatography at the sulfonamide intermediate stage. The relative stereochemistry of **7** was assigned from X-ray crystallographic study of the corresponding *tert*-butyl sulfonamide single crystal as *erythro*.[5] This *erythro* isomer exhibits a high level of activity against several annual and perennial paddy field weeds and low activity against transplanted rice. It is particularly active against barnyardgrass, which is the main problem weed in paddy fields. Of the two diastereoisomers, the *erythro* form (**7**) is more active than the *threo*- form **8**.

We next focused on the effect of aromatic ring substitution on herbicidal activity. A fluorine substituent at the 6-position on the phenyl ring gave compound **9** with similar activity to that of compound **7**. However, introduction of the strongly electron-donating dimethylamino group at this position (compound **10**) resulted in reduced activity. Introduction of a strongly electron-withdrawing group in the 5-position (compound **11**) resulted in a complete absence of activity at 50 g ha^{-1}, while the introduction of the electron-donating methoxy group at position **5** (compound **12**) resulted in moderate activity. A (electron-withdrawing) fluoro group at positions such as **4** and **5** in the phenyl ring resulted in diminished activity (compounds **13** and **14**, respectively).

In conclusion, fluoroalkyl hydroxymethylsulfonylureas represent a new class of sulfonylurea herbicide with high activity. Of the various derivatives tested, the *erythro*-fluoroethyl compound (coded K11451) showed excellent herbicidal activity against several annual and perennial paddy weeds, including barnyardgrass, and caused little damage to transplanted rice.

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Herbicidal and biological characteristics of a new benzenesulfonylurea compound K-11451 under submerged paddy conditions

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Abstract: The new benzenesulfonylurea K-11451, an α-hydroxy-β-fluoropropyl- compound, applied at 3–9 g ha^{-1}, controlled annual and perennial weeds grown in submerged paddy soil under greenhouse conditions. It effectively controlled barnyardgrass at growth stages varying from pre-emergence to the five-leaf stage. The compound inhibited acetolactate synthase, I_{50} values for the enzyme isolated from barnyardgrass and rice being 56 and 67 nM, respectively. K-11451 inhibited the growth of rice when it was transplanted at a shallow depth (0–1 cm) and water leaching from the paddy soil was high (3–5 cm per day). With a water depth of 3 cm, the compound appeared to move readily down into the paddy soil and had the relatively short half-life of 15.2 days under submerged paddy conditions. A mixture of K-11451 + mefenecet + daimuron (9 + 250 + 250 g ha^{-1}) controlled almost all weeds in the paddy field without injury to rice, so that the combination could be used as a 'one-shot' herbicide in rice culture.

Keywords: acetolactate synthase; barnyardgrass; benzenesulfonylurea; daimuron; leaching; mefenecet; one-shot herbicide; rice

Sulfonylurea herbicides are highly active at low application rates, control a wide spectrum of weeds and have favourable toxicological properties. They are also safe to use in a number of major crops including rice. The sulfonylureas, along with imidazolinones and triazolopyrimidines, are acetolactate synthase (ALS) inhibitors,[1] KIH-2023[2] and LGC-40863[3] being examples of success in this area.

Barnyard grass (*Echinochloa* spp) is one of the most troublesome weeds in paddy fields world-wide; infestations with this weed cause severe yield loss and quality reduction in rice culture[4] so that rice growers anxiously await a new herbicide to control it, as well as other annual and perennial weeds.

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